

POTENTIAL APPLICATIONS OF LIGNIN AND ITS DERIVATIVES FROM LIGNOCELLULOSIC BIOMASS – A REVIEW

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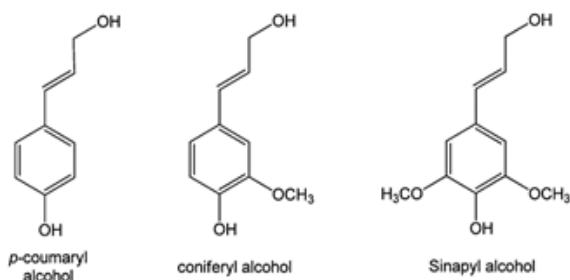
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Graphical abstract



Abstract

Lignin is the second most abundant component of lignocellulose biomass after cellulose with annual production of 70 million tons. Lignin constitutes between 15 to 40 percent of its dry weight, with varying composition in woody plants such as softwood (18-25%) and hardwood (27-33%), and non-woody plant such as grass (17-24%). The polyphenolic polymer is made up of three monolignols such as coniferyl alcohol, sinapyl alcohol, and p-coumaryl alcohol that later forms an aromatic structure consisting of guaiacyl, syringyl, and p-hydroxyphenyl. The highly branched three-dimensional structure is both complex and recalcitrant, hence making its utilization difficult. However, the polymeric lignin can be extracted by various methods such as physical, chemical and biological. The extracted lignin has high potential to be converted into monomeric aromatic derivatives that could serve as a building block for chemical synthesis, biomaterials, bio-oils, wastewater treatment and food industry. The conversion involves several methods such as alkaline nitrobenzene, pyrolysis, catalytic technology, combustion, gasification, hydrocracking and oxidation.

Keywords: Lignocellulosic biomass, polyphenolic, cellulose, hemicellulose, lignin, lignin derivatives, extraction

Abstrak

Lignin merupakan komponen biojisim lignoselulosa yang kedua terbanyak selepas selulosa dengan pengeluaran tahunan sebanyak 70 juta tan. Lignin mengandungi berat kering antara 15 – 40 peratus dengan kepelbagaian komposisi dalam tumbuhan berkayu seperti tumbuhan berkayu lembut (18-25%), tumbuhan berkayu keras (27-33%), dan tumbuhan tidak berkayu seperti rumput (17-24%). Polimer polifenolik terdiri daripada tiga monolignol iaitu alkohol koniferil, alkohol sinapil, dan alkohol p-kumaril yang kemudiannya membentuk struktur aromatik yang mengandungi guaiasil, siringil dan p-hidroksifenil. Struktur tiga-dimensi bercabang yang kompleks dan rekalsitran menyebabkan ianya sukar untuk dimanfaatkan. Walaubagaimanapun, lignin polimerik boleh diekstrak dengan menggunakan pelbagai kaedah seperti kaedah fizikal, kaedah kimia, dan kaedah biologi. Lignin yang telah diekstrak mempunyai potensi yang tinggi untuk ditukarkan kepada monomer aromatik terbitan yang boleh dijadikan sebagai bahan asas untuk

sintesis kimia, bio-bahan, bio-minyak, rawatan air sisa, dan industri makanan. Penukaran melibatkan beberapa kaedah antaranya menggunakan nitrobenzena beralkali, pirolisis, teknologi mangkinan, pembakaran, penggasan, proses hidrokrak, dan pengoksidaan.

Kata kunci: Biojسيم lignoselulosa, polifenolik, selulosa, hemiselulosa, lignin, lignin derivatif, pengekstrakan

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1.0 INTRODUCTION

Various renewable energy sources have received major attentions due to their inexpensiveness, and abundant availability worldwide. Among these, lignocellulosic biomass is the most abundant and renewable source in the world [1-3]. Approximately 2.2×10^{11} t of dry lignocellulosic biomass was estimated to be produced per year but only 1.2×10^{10} t dry tons are available on a sustainable basis [4, 5]. Lignocellulosic biomass refers to woody and non-woody dry matters that composed of three major components namely cellulose (35-55%), hemicellulose (20-40%) and lignin (15-30%). These three lignocellulose components are chemically bounded to one another by covalent bonds in plant cell walls [6, 7]. Among the three biopolymers, lignin is the second most abundant organic compound after cellulose and is also the most resistant component due to their hydrophobicity properties. Carbohydrate polymers such as cellulose and hemicellulose consist of different types of six and five carbon sugars that are tightly bounded to lignin. Generally, the composition of lignocellulosic biomass is highly dependent on the types of biomass, locality, climatic conditions and the soil where it grows [6, 8].

More than 70 million tons of lignin are produced annually [9] and is the largest non-carbohydrate fraction in lignocellulosic biomass [10]. Lignin can be found as an industrial residue from pulping, paper industry and biofuel production [11, 12]. However, it remains as underutilized feedstock in different fields such as pulping and paper industry [13-15]. The processes widely used in the current industry were produced from two types of lignin, lignosulfonate (sulphite pulping process) and kraft lignin (kraft pulping process) [16, 17]. However, only less than 2% of those lignin was utilized while the rest was burned as a low-value fuel for energy which might lead to environmental pollution and waste of aromatic resources [9]. Kraft lignin in the form of black liquor is the primary source in industrial factory which represents approximately 90% of the total amount of lignin produced [18]. The composition products from lignin extraction rely on the plant source, plant species and generation of lignin precursors in plant biosynthetic pathways.

The technical lignin consists of several functional groups such as phenolic hydroxyl, carboxylic, carbonyl and methoxyl groups [19]. The linkages of complex

polyphenolic lignin structures are divided into two types which are ether linkages such as β -O-4 (aryl ether), α -O-4 (aryl ether), and 4-O-5 (diaryl ether) and condensed linkages such as β -5 (phenyl-coumaran), 5-5 (biphenyl), β -1 (1,2-diarylpropane), and β - β (resinol) [20, 21]. These chemical bonds highly depend on the lignin source and delignification process to produce the specific products. Most of the biorefinery schemes focus on the usage of cellulose and hemicellulose while lignin remains underutilized and considered as waste. However, the chemical structure of polymeric lignin could be an excellent source of valuable chemicals and other beneficial products if it could be break into smaller molecular units and useful physicochemical properties.

Therefore, the main purpose of this review paper is to clarify and provide short overview about the applications of lignin and its derivatives from different types of lignocellulosic biomass. In summary, this review provides the extended insights on lignin recovery, factors influencing the recovery of lignin from different sources and the utilization of lignin derivatives in various fields such as metal ion removal and bio-sorbent, antimicrobial and antioxidant in textile and food packaging, phenol-based resin, corrosion inhibitor, aviation fuel, and vanillin flavour production.

2.0 LIGNOCELLULOSIC BIOMASS: TYPES AND COMPOSITION

Plant cell wall mainly consist of three major components, cellulose, hemicelluloses and lignin. Table 1 compares the composition of lignocellulose components in both woody and non-woody plants. Woody plants consist of softwoods (gymnosperms) and hardwoods (angiosperms), while non-woody plants (herbaceous crops) such as grasses are angiosperms. In general, cellulose consists of 40-50% of the dry weight, hemicellulose consists around 25-35%, lignin consists 15-30% and extractives 1-5% [8, 22, 23] (Table 1). The major component of lignocellulosic biomass is cellulose, which consist of β -1,4-linked glucose molecules in a straight chain. The second most abundant lignocellulose component is hemicellulose, a branching structure comprised of both hexose (C-6) and pentose (C-5) sugars such as arabinose, glucose, mannose and xylose. The third component is lignin with

a three-dimensional structure made up of phenolic and non-phenolic components. Table 2 shows the cellulose, hemicellulose and lignin that further explain the criteria of these three lignobiomass. The

composition of these lignocelluloses highly depends on its sources whether it was deriving from the hardwood, softwood or grasses [24, 25].

Table 1 Composition of cellulose, hemicelluloses and lignin contents (as weight percent of dry biomass) lignocellulosic materials

Types of lignocellulose	Feedstock	Cellulose (%)	Hemicellulose (%)	Lignin (%)	References
Hardwoods	Oil palm empty fruit bunch	37-39	21-31	19-24	[26]
	Oil palm frond	45.2	17.5	22.2	[27]
	Oil palm trunk	45.81	17.74	24.49	[28]
	Palm kernel shell	30.1	21.4	47.3	[29]
	Oil palm fibre	42.7-65	17.1-33.5	13.2-25.31	[30]
	Sawdust	17.4	4.2	61.8	[31]
	Coconut husk	39.31	16.15	29.79	[32]
	Arecanut husk	28.3	24.6	24.7	[33]
	Hybrid Poplar	42-49	16-23	21.5-27.2	[34]
	Pine	48.6	10.5	25.3	[35]
	Eucalyptus	52	24	17	[36]
	Red maple	37.7	22.1	26	[34]
	Rapeseed (stem and leaves)	21.7	3.3	3.2	[37]
	Pea pod	26	20.5	3.92	[38]
	Almond shell	36.3	12.1	47.4	[39]
Fir	38	30	24	[36]	
Softwoods	Rice straw	28	55	11	[40]
	Rice husk	36-40	12-19	17-19	[41]
	Sugarcane bagasse	36.4	20.1	29.9	[42]
	Sweet sorghum bagasse	45.03	30.17	24.4	[43]
	Wheat straw	29-35	26-32	16-21	[24]
	Corn stover	38	26	19	[24]
	Corn cobs	41.27	46	7.4	[45]
	Corn straw	49.3	28.8	7.5	[46]
	Cotton stalks	36	21	28	[47]
	Coffee husk	26.5	25.5	33.5	[48]
	Sorghum straw	32-35	24-27	15-21	[25]
	Barley straw	36-43	24-33	6.3-9.8	[25]
	Barley hull	34	36	13.8-19	[25]
	Sunflower stalks	54.5	9.7	13.9	[49]
	Miscanthus	44	18	25.1	[50]
	Pinus banksiana	38.8	23.6	20.4	[51]
	Brewer spent grain	17-25	25-35	8.0-28.0	[52]
	Banana (Rachis)	26.1	11.2	10.8	[53]
	Banana (Pseudostem)	20.1	9.6	10.1	[53]
	Bamboo	47.2	23.9	25.3	[54]
Grass	Lemongrass leaves	29.9-35	28.5-47	7-11	[55]
	Grasses	25-40	25-50	10-30	[25]
	Switchgrass	31-38	32	17-21	[50]
	Wild rice grass	28.5	13	31	[56]

Table 2 The criteria of cellulose, hemicellulose and lignin

	Cellulose	Hemicellulose	Lignin	References
Subunits	Composed of repeated units of cellobiose (two anhydrous glucose rings)	Composed of pentoses (D-xylose and D-arabinose), hexose (D-mannose, D-glucose and D-galactose) and sugar acids	Composed three types of aromatic units, Guaiacyl (G), Syringyl (S) and p-hydroxyphenyl (H)	[26]
Bonds between the subunits	β -1,4-glycosidic bonds	β -1,4-glycosidic bonds in main chains; β -1,2-, β -1,2-, β -1,6-glycosidic bonds in side chains	Variety of ether and carbon-carbon bonds. The predominant linkage is β -O-4 linkages	[27]-[29]
Degree of polymerization	~5000 - 15,000	~ 70-200	Several hundred to tens of thousands	[30]
Percentage of major component	40-60%	20-40%	10-30%	[31], [32]
Polymer morphology	Three dimensional linear molecular Composed of the crystalline region and the amorphous region	Three dimensional inhomogenous molecular with mainly amorphous region	Inhomogeneous molecular with tightly packed and crystalline region	[33], [34]

3.0 LIGNIN: STRUCTURE, EXTRACTION AND FACTORS AFFECTING RECOVERY

Despite its abundance, lignin as a natural renewable biopolymer is highly underutilized [35]. Lignin accounts for 15–30% dry weight of lignocellulose. It is estimated that around 3×10^{11} metric tons of lignin are produced but, only 2×10^{10} tons is actually being biosynthesized per year [36]. However, this value is only an estimation since there is no reliable statistics on lignin productions. It is mostly being burnt to be utilized as fuels immediately after pulping process [37]. The following sub-section will review the chemical structure of lignin, its extraction process and factors affecting its recovery.

3.1 Chemical Structure

Lignin is a complex three-dimensional structure that are formed from dehydrogenative radical polymerization of p-hydroxycinnamyl, coniferyl and sinapyl alcohols. Each of these monolignols results in a different types of lignin units called p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units, respectively [38] (Figure 1). Guaiacyl lignin composed principally of coniferyl alcohol units, while guaiacyl syringyl lignin contains monomeric units from coniferyl and sinapyl alcohol. The ratio of G: S: H units varies in between

softwood and hardwood plants. In general, guaiacyl lignin is found in softwoods (Figure 3) while guaiacyl-syringyl lignin is present in hardwoods (Figure 4). Different proportions of syringyl, guaiacyl or p-hydroxycoumaryl units present contribute to the variety of molecular weight of lignin [39].

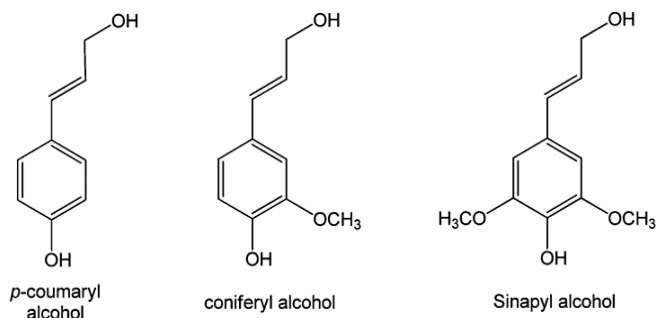


Figure 1 Structures of the building block monomeric aromatic precursors of lignin [40]

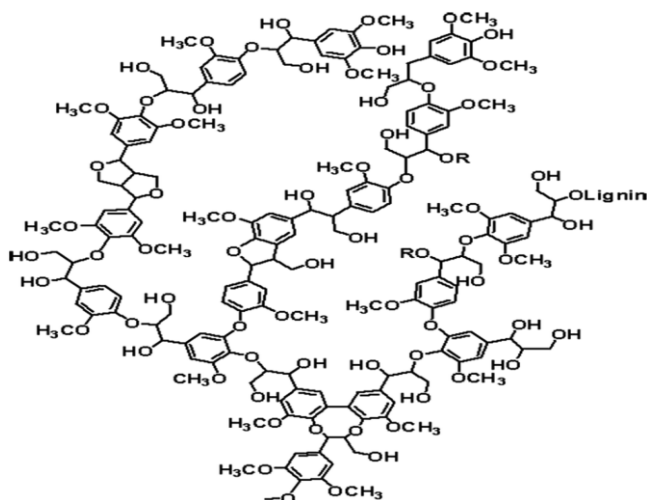


Figure 2 The complex structure of lignin in plant [41]

The lignin macromolecule contains various functional groups such as methoxyl groups (OCH_3), phenolic hydroxyl groups (OH), benzyl alcohol groups, carbonyl groups ($\text{C}=\text{O}$) and some terminal aldehyde groups in the side chain (Figure 2). Lignin are basically connected with carbohydrates components (in particular with hemicelluloses) by covalent bonds at two different sites which are α -carbon and C-4 in the benzene ring that forms lignin carbohydrate complexes (LCC). The most notable reaction site in lignin is the OH group, which is the case for both phenolic and alcoholic hydroxyl groups [26].

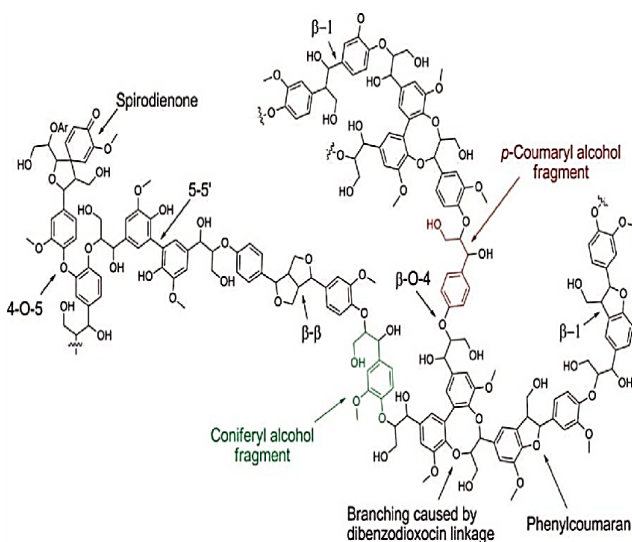


Figure 3 Schematic representation of a softwood lignin structure [42]

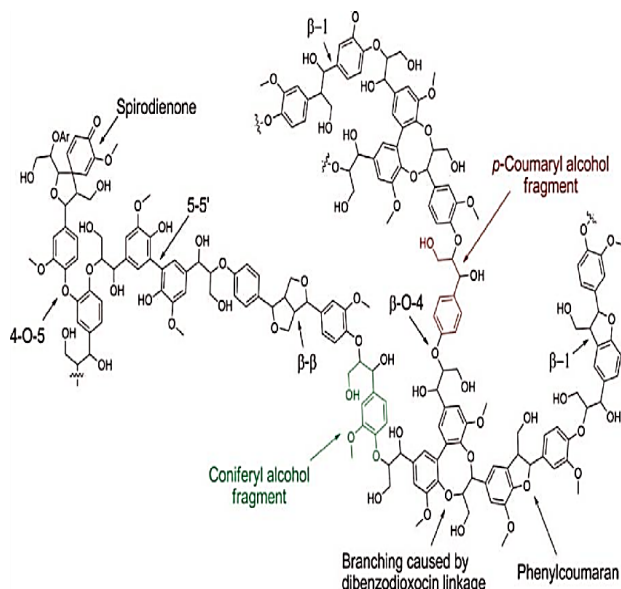


Figure 4 Schematic representation of a hardwood lignin structure [42]

3.2 Types and Extraction Process

The removal of lignin from lignocellulose biomass is beneficial in various processes such as enzymatic hydrolysis for sugar production. In enzymatic hydrolysis, the presence of lignin would impede enzymatic access to cellulose and hemicellulose. It widely recognised that lignin acts as a cement that hold carbohydrate material in plant cells together, hence its removal is crucial. Various studies have explored lignin extraction by different methods involving physical, chemical and enzymatic. The extraction process causes structural modifications to the lignin that converts it from solid biomass to the liquid phase during the aqueous pre-treatments. Extraction of lignin from lignocellulosic material are performed with at least physical and chemical changes in the extracted lignin, so that it can be utilize further and accepted as representative of native lignin. The natural colour of lignin is either colourless or pale yellow but it changes to brown or dark brown when processed with acid or alkali [43].

Some of the commonly used method of lignin extraction are sulphuric acid pre-treatment, sodium hydroxide pre-treatment, steam explosion [44], organosolv, alkaline-isolation, kraft process and ionic liquids [39]. These methods are often incorporated as part of the pre-treatment process of the ligocellulose biomass. An efficient lignin extraction would be able to remove hemicelluloses and enable the determination of biomass saccharification under various types of alkaline and acidic pre-treatments which leads to a significant alteration of cellulose crystallinity [45]. Different types of lignin extracted from different sources and different methods such as klason method, ionic liquid method, organosolv method and

cellulolytic enzyme method together with their benefit and challenges are summarised in Table 3.

3.2.1 Klason Lignin

Klason method is one in all the method that are applied frequently to determine the content of lignin. The comparison study by using six types of lignocellulosic biomass involving wheat straw, rice husk, corn straw, sugarcane baggase, wood chips and elephant grass were investigated to determine the efficiency of lignin extracted by using two different methods which are the Klason method (sulphuric acid, H_2SO_4) and the Willstatter method (hydrochloric acid, HCl). They reported that lignin extraction from the Klason method yielded higher recovery of lignin compared to the Willstatter methods. This is due to the lower pH used in the Klason method (pH 2), which is considered more effective for hydrolysis than the Willstatter method (pH 4).

In another study, lignin extracted from Moso bamboo, Chinese tallow tree wood, switchgrass and pine wood produced high Klason lignin content which is greater than 75% and managed to maintain their natural structure [46]. In the study, the extracted lignin was subjected to a novel delignification method using microwave energy in a binary glycerol/methanol solvent, and which were further applied in the fabrication of polylactic acid [47]lignin composites. The extraction efficiency highly depends on the target products and the process can be stimulate by the addition of acid, alkali, hydrogen peroxide or alcohol [48].

Microwave-assisted extraction has been reported as an effective technology in separating the components of lignocelluloses because it can reduce the energy requirements. This study successfully extracted over 80% of lignin at 109°C in 60 minutes while the prolonged time to 120 minutes did not induce any enhancement of the solubilisation rate. The increase of extraction time and temperature enhance the release of methoxy, OCH_3 groups in lignin which is mainly caused by demethylation reaction under drastic conditions. Phenolic hydroxyl content in lignin increased due to the cleavage of the linkages between lignin units (mainly β -O-4 linkages) during the extraction process which formed new phenolic end groups and at the same time increased the phenolic hydroxyl content in the sample. Microwave-assisted extraction is applied during the mild acidolysis step, which severely cleaves lignin-carbohydrate and results in a greater lignin yield and purity [49].

Lignin removal from oil palm trunk by using microwave-alkali method resulted as high as 22.38% which is equivalent with 13.87 g/100 g compared with 17.87g / 100 g in raw oil palm trunk biomass. However, the removal of lignin reported in this study is lower since the trunk of oil palm trees contain higher lignin percentage and thus require harsher conditions to achieve higher lignin removal. The longer reaction time did not give any significant difference in terms of

lignin contents, therefore shorter duration of treatment and temperature play significant roles in achieving maximum lignin removal in the sample [50]. From the elemental analysis, no nitrogen was detected which shows that the extracted lignin is not being contaminated by protein. Molecular weight and lignin bond carbohydrate also decreased when using microwave technique [48].

The main drawback of klason lignin method is the contamination by carbohydrates residues if not performed well during the pH adjustment especially for herbaceous samples. This is because, herbaceous samples have higher lignin contents and appearance of waxes from cutin when leafy materials were proceeding for analysis especially in forage plants. Therefore, one of the proposed studies found that immature wood, will be pre-extracted with ethanol-benzene prior to proteolytic enzyme treatment and diluted sulphuric acid before using klason method to obtain acid insoluble lignin residue [51]. Lignin residue extracted after filtration process by using klason method contained ash, which make their quantifications harder compared to the gravimetric method. However, klason lignin concentrations were reported to be higher than those extracted in acetyl bromide method. But, other plant materials such as tannins and cutin might interfere with sulphuric acid lignin values [52].

3.2.2 Ionic Liquid Lignin

Ionic liquid pre-treatment is an eco-friendly method. Its non-flammable capacity can enhance the accessibility of cellulolytic enzymes to the biomass by reducing the lignin content and the crystallinity. Ionic liquids have the ability to dissolve organic (polar and non-polar), inorganic and polymer compounds either completely or into individual fractions. Ionic liquids have the potential to dissolve cellulose which may have a practical advantage for enzymatic hydrolysis process of cellulose [53].

Lignin produced from ionic liquid treatment is reported to have better properties and characteristics than lignin obtained by conventional processes [54]. The ionic liquid can dissolve the biomass owing to the strong hydrogen-bonding of certain ions such as weakly solvated chloride anion in pure 1-butyl-3-methylimidazolium chloride ([Bmim] Cl). These anions can extensively disrupt the hydrogen-bonding present in the three-dimensional network of lignocellulosics, leading to either dissolution of wood or selected individual components based on the nature of the anion [55].

The characterization of extracted lignin from ionic liquid method shows less structural changes and degradations in *P. nigra* (Poplar), *C. sempervirens* (Cypress) and *Gramineae Saccharum officinarum* L. (baggase) compared to dioxane method. The production of lignin from empty fruit bunch using 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) ionic liquid in the presence of sulphuric acid, H_2SO_4 as a catalyst was also reported by [56]. The extraction of

lignin from triticale, wheat straw and flax shives were done using 1-ethyl-3-methylimidazolium acetate ([emim]Ac) ionic liquid at various temperatures between 70-150°C for 0.5 to 24 hours. The highest extracted lignin was recovered by acid precipitation from triticale straw was 52.7 %, and this was achieved at 150°C after 90 minutes [57].

A common property of cellulose-dissolvable IL is their ability to break down the extensive inter and intramolecular hydrogen bonding network. With the dissolution of cellulose, more and more lignin was being exposed and became accessible to the solvent and thus dissolved, resulting in more efficient extraction of lignin. IL with stronger capacity for lignin extraction also provides higher cellulose digestibility of the residue. Higher temperature increased the solubility of cellulose and lignin in various IL including 1-butyl-3-methylimidazolium chloride ([bmim]Cl), N, N-dimethylethanolammonium acetate, DMEF, N, N-dimethylethanolammonium acetate, DMEAA, N, N-dimethylethanolammonium glycolate, DMEAG, N, N-dimethylethanolammonium succinate, DMEAS. It also accelerated the diffusion of ILs into lignocelluloses, resulting in more lignin dissolved in the ionic liquid and provides a more efficient extraction of lignin.

The lignin extracted from different types of ionic liquid were studied by [58] by using corn stalk as the lignobiomass raw material including N-methyl-2-pyrrolidonium chloride ([Hnmp]Cl), N-methyl-2-pyrrolidonium methane sulfonate ([Hnmp]CH₃SO₃), N-methyl-2-pyrrolidonium hydrogen sulphate ([Hnmp]HSO₄) and N-methyl-2-pyrrolidonium dihydrogen phosphate ([Hnmp]H₂PO₄). The lignin extracted from ([Hnmp]Cl) and ([Hnmp]CH₃SO₃) at 90°C for 30 minutes were reported to be the highest among the ionic liquid tested which are 85.94% and 56.02 % of the original lignin respectively. The yield of lignin pre-treated with ionic liquid is higher than ionic liquid/ water due to the decreased dissolution of lignin when water was added. The presence of strong hydrogen bond basicity in ionic liquid were weakened by the hydrogen-bonding network of the polymer chains apart from providing good solubility for lignin. Anion Cl⁻ and CH₃SO₃⁻ made it more effective by disrupting inter and intra-molecular hydrogen bonding in polymers and the accelerated lignin solution.

The lignin extracted from ionic liquid methods has little structural change, more uniform and larger average molar mass compared to kraft lignin. Lignin isolated from ionic liquid methods can be easily recovered using centrifugation or simple filtration which results in a lignin-free ionic liquid with lacks of cellulosic residues and substantially depolymerized lignin to be used in the valorisation process. Water used as the solvent to wash lignin from ionic liquid can avoid the higher operating expenses. The lignin extracted was reported to comprised major units of lignin such as syringyl, guaiacyl and p-coumarate ester which can be further process to produce other products [59]. However, the main drawback of the ionic liquid is the cost recyclability issues which limit its application at commercial scale. Another challenge

for ionic liquid is difficulties in separation of low molecular weight of lignin than the precipitation of high molecular weight of cellulose, hemicelluloses and lignin due to the intrinsically higher solubility that accompany low molecular weight of solutes [60].

3.2.3 Organosolv Lignin

Organosolv process involved many types of solvents such as ethanol, acetone, ethylene glycol, acetic acid, esters, soda-amine and ethanol alkali. The conventional non-organic based alkaline kraft and acidic sulphite based on full chemical pulping will cause the disastrous environmental pollutions. The lignobiomass raw material is separated into three fractions: cellulose rich-fractions, water soluble fractions consisting of hemicelluloses degradation products and a large fraction of dissolved sulphur-free lignin during organosolv pulping. The major types of bonding, β-aryl ether bonds are cleaved resulting in the formation of phenolic hydroxyl groups in the lignin macromolecule [61].

The different organosolv methods to evaluate the extraction capacity, extraction efficiency and antioxidative property of lignin were studied by [62]. They used four different ratios of solvents to delignified *Acanthopanax senticosus remainder* which contains a large proportion of cellulose and lignin including acetone–acetic acid–water, 1,4-butanediol–acetic acid–water, ethanol–acetic acid–water and acetic acid–water method. This study concludes that the holocellulose and lignin content was in a significantly inverse correlation. This is because acetic acid used to delignify lignobiomass can penetrate into fibres which cause the lignin removal and the degradation of carbohydrate. Higher lignin yield was extracted from triticale straw by using 92% ethanol with 0.64N of catalyst, H₂SO₄ at 148°C as reported by [63].

Microwave-assisted organosolv succeed in maintaining the content of lignin as integral as possible while degrading the cellulose and hemicelluloses in lignobiomass materials. [61] investigated beech wood lignin by using 50:50 ethanol water mixtures with a presence of sulphuric acid as a catalyst and their obtained yields of total lignins were between 91.4-94%. Organosolv (acetic acid/formic acid) under acidic condition induced the delignification by cleaving the bonds between lignin and hemicelluloses in material waste (pine straw, wheat straw, alfalfa and flax fiber) as reported in a study by [64]. The presence of hydrogen peroxide as an oxidizing agent and organic acid will enhance the delignification by dissolving the lignin in formic acid/acetic acid media. Hydroxonium ion, OH⁺ is a strong electrophilic agent produced in the extraction stage of peroxy acid in acidic medium and will react with lignin during the delignification process.

Lignin removals from cornstalks were hydrolyzed using organosolv method under atmospheric pressure and low temperature without any catalyst. The delignification of lignin from a solid lignin-rich industrial waste (residue of enzymatically hydrolyzed cornstalks)

reported after extraction with 65-75% of ethanol-water, 1,4-dioxane-water and tetrahydrofuran-water was 34.5%, 41.8% and 53.7% respectively [65]. Higher lignin yield extracted from air dried bioethanol residue converted from steam exploded cornstalk using benzyl alcohol, dioxane and ethanol was 71.55 %, 74.14% and 44% respectively [66].

The delignification parameter was determined based on value differences between the Klason lignin contained in initial material and lignin in the extracted solid residue. They reported that the organic solvent contained lower than 35% vol. in the extraction media resulted in low delignification (less than 10%). The tetrahydrofuran-water mixtures led to the largest hydrophobicity which disrupted most of the H-bonded network of water. The findings from this study conclude that the closer the Hildebrand solubility parameter (delta-values of the organosolv mixed solvent approached that of lignin) the greater solubility of lignin was observed, thus leading to a greater degree of delignification.

Lignin extracted from organosolv study composed of mostly aromatic rings with various branching [64] and has high purity. It also consists of a limited amount of residual carbohydrates and minerals, sulphur-free [67], low molecular weight, and little ash [68]. In comparison to kraft and sulphite lignin, organosolv lignin is better since it is highly phenolic, highly hydrophobic and contains less contaminants especially sulphur which can easily be eliminated during heating [69]. In organosolv process, the residual and dissolved lignin fractions after the pre-treatment shows abundance of phenols and carboxylic acids but lower aliphatic carbon content which make lignin suitable to be used as antioxidants. The structure of the lignin produced is also close to those of the native lignin.

However, the major drawback of the volatility and harsh acidic conditions of this technique results in the toxicity, corrosion and pollution. Liquid stream containing lignin and hemicelluloses-derived products produced after organosolv treatment needs to undergo purification step to recover a much higher lignin value [70].

3.2.4 Cellulolytic Enzyme Lignin (CEL)

Cellulolytic enzyme lignin (CEL) refers to the lignin from pretreated substrates which have been enzymatically hydrolysed to remove remaining carbohydrates prior to extraction of lignin-rich fraction by using aqueous dioxane. Rate determining step for preparation of cellulolytic enzyme lignin (CEL) depends on the efficiency and accessibility of cellulase to the limited adsorption sites on crystalline cellulose. It is shown that, cellulase readily hydrolyses the more accessible amorphous portion of cellulose but is proven less effective in degrading the crystalline portions. Therefore, higher crystallinity of cellulose shows higher resistance to enzymatic hydrolysis. Decreasing the crystallinity of cellulose is essential to control more efficient cellulase hydrolysis of lignocellulosic materials

in order to produce higher yield of cellulolytic enzyme lignin (CEL) [71].

Cellulolytic enzyme lignin is reported as the representative preparations from hardwood lignocellulosic lignin as the S/G ratios in the CEL is identical to those in lignin in-situ. [72] reported that the preparation of CEL by using Cellulysin, a crude cellulase from *Trichoderma viride* which also contains hemicellulase activities. Klason lignin obtained was around 105 % indicating the presence of some contaminants in their preparations. The main lignin substructures reported from BSG samples include β -O-4' alkyl-aryl ethers (77-79% of all interunits linkages), β -5' phenyl-coumarans (11-13%), β - β' resinols (5-6%) and 5-5' dibenzodioxocins (3-5%). [71] also investigated the isolation of cellulolytic enzyme lignin (CEL) from Basswood (hardwood) and loblolly pine (softwood) by using cellulysin cellulase (containing hemicellulase activities) from *Trichoderma viride*. Klason lignin yield remained from DMSO/N-methylimidazole after enzymatic treatment with cellulase resulted in 45.8% and 35.3 % for basswood and loblolly pine respectively compared with untreated materials which only resulted in 36.5 % and 30.5%.

Rate determining step for preparation of cellulolytic enzyme lignin (CEL) depends on the effectiveness and accessibility of cellulase to the limited adsorption sites on crystalline cellulose prior to the extraction step by using aqueous dioxane treatment. It is shown that, cellulase readily hydrolyses the more accessible amorphous portion of cellulose but proven less effective in degrading the crystalline portions. Therefore, higher crystallinity of cellulose shows higher resistance to enzymatic hydrolysis. Decreasing the crystallinity of cellulose is required to regulate more efficient cellulase hydrolysis of lignocellulosic materials in order to obtain higher yield of cellulolytic enzyme lignin (CEL) [71].

The enzymatic hydrolysis of lignobiomass substrates for biochemical conversion of renewable biomass into valuable products involves three types of interactions which are electrostatic interactions, hydrophobic interactions and hydrogen bonding between cellulase and lignin. Hydroxypropylation of free phenolic hydroxyl groups on lignin plays an important role in enzymatic hydrolysis process. The residual lignin and softwood hydrolytic lignin had shown strong inhibition on endoglucanase production but less inhibition on xylanase and beta-glucosidase [73].

Lignin isolation by using enzymatic hydrolysis had been used since 1981. The pulp carbohydrates were depolymerised and dissolved by cellulase and hemicellulase enzymes, leaving a lignin residue behind. Enzymatic hydrolysis remains the linkages between lignin and carbohydrates. Even though this method produces high recovery of lignin, it has disadvantages of containing significant amounts of carbohydrates and some protein residues in their fractions [74].

The lignin recovery from this types of isolation has been structurally similar to milled wood lignin (MWL) with less degradation, lower amount of carbohydrates

and higher yields (95% of acid insoluble lignin, AIL) as reported by [75]. Cellulase has been absorbed by the

lignin via hydrophobic interactions, ionic bond interactions and hydrogen bond interactions.

Table 3 Non-biological and biological lignin recovery methods

Recovery methods	Biomass	Benefits	Challenges	Products	References
Klason and Willstatter	Wood chips, rice husk, sugarcane baggase, corn straw, elephant grass	Accurate and reproducible, sulphuric acid correct the ash contamination in sample	Does not represent the original lignin, protein contamination	Klason lignin, acid soluble lignin, carbohydrates	[52], [76]
Organosolv	Wheat straw, Pine straw, Alfalfa, Flax fiber	Low carbohydrate and ash content, sulphur-free and high purity, low molecular weight of lignin, lignin produced has high pore volume which enhances the solubility in solvent	Require acidic conditions for effective delignification rate:	Cellulose, hemicellulose, lignin, phenolic compounds, Sugar	[64] [77] [78]
Ionic liquid	Triticale straw, southern yellow pine, Oil palm empty fruit bunch, Red oak	Lignin is chemically unaltered	IL has corrosive properties and high viscosity, Lignin has little structural change	Cellulose, hemicellulose, lignin, sugar	[56, 79, 80]
Commercial cellulase and Protease	Sweet gum, Douglas-fir chips, basswood	Lignin structure is similar to milled wood lignin (MWL) with less degradation	Lignin contains some carbohydrates and proteins impurities	Cellulose, hemicellulose, lignin, sugars	[71], [72], [75]

3.3 Factors Affecting Lignin Recovery

There are several factors which affect the amount of lignin extracted from lignocellulosic biomass. The lignin recovery from different sources may be related to their origin, methods and condition of extraction, cycles of extraction, pH and types of solvent used during the process.

3.3.1 Origin

The chemical structure and yield of lignin extracted from lignocellulosic biomass depends on several factors including their botanical origin, biomass resources, the environmental conditions of growth and the conditions applied during the extraction and purification processes during the treatment [81-84]. The variations occur in different species of plants with respect to the generation of lignin precursors in plants or tree biosynthetic pathways [18]. [47] reported that there are different monomers and distributions of bond linkages present in the lignin extracted from different types of coconut shells, walnut shells, peach pits, and olive pits even though they were being extracted by using the same formic acid procedure.

3.3.2 Method and Condition of Extraction

Application of different methods influence the composition of lignin yield and the functional groups

presence in the structure [85]. Research by [48] reported that the yield of lignin, molecular weight and thermal stability were increased when supplemented with acoustic energy and solvents compared to the fraction without ultrasonic irradiation due to the intensification of mass transfer, improvement of the effect of penetration of solvent into the plant tissue and capillary permeability. Another study done by the same author mainly to investigate the influence of microwave radiation towards lignin yields. They proved that when applying microwave radiation during the extraction process, the molecular weight of the lignin increased while there are also decrement reported in bound carbohydrate content. Various conditions applied by researchers in different techniques of extraction could affect the molar mass, functionality, cross-linking and density of the lignin obtained. The particle size of biomass also influence the amount of lignin extracted from lignobiomass. A smaller particle size of biomass contributes to a more effective lignin extraction as reported by [76]. The ability of solvent to penetrate into the biomass structure is reduced when the particle size is larger and the surface area is small [86].

3.3.3 Extraction Cycle

The cycles of extraction process also influenced the amount of lignin extracted from the lignocellulosic

biomass. Research done by [87] reported that, molar mass lignin obtained from the first cycle of extraction was lower than at the end of the cycles. This is supported by the fact that the small parts of the molecule are easier to remove from the outer layer of the wood particles.

3.3.4 pH Value

The pH value during the extraction also influence the amount of lignin extracted. Lower pH used in the hydrolysis produced higher lignin amount as proven in the method used for Klason and Willstatter approach. Klason method utilizes sulphuric acid solvent at pH 2 while Willstatter method utilizes hydrochloric acid at pH 4 during the hydrolysis. Lignin extracted from Klason method shows a much higher percentage than Willstatter method. The recovery of lignin extracted from all types of biomass by different methods is always significantly influenced by the concentration of catalyst either acidic or basic. Increasing the concentration of base induced the recovery of lignin extraction [88]. The average molar mass of lignin extracted depends on the alkali concentration used during the extraction process. However, the amount of lignin did not increase when alkali neutralisation took place in the reaction [87].

3.3.5 Types of Solvent

Lignin yields also depends on the solvent used during the extraction process. The concentration of alkali will reduce the complexity and molecular size of acetylated lignin by disrupting the chemical bonds present in the lignin, cellulose and hemicelluloses structures. The solvents used promote the impregnation of vegetal tissue which leads to solubilisation of lignin fragments. The intermediate carbonium ions produced will react with an electron-rich carbon to form stable carbon-carbon linkages leading to the condensation of lignin [89]. Incomparable new solvent of ionic liquid which are salts comprised of large organic cations and smaller inorganic or organic anions give higher potential to disrupt the strong linkages between cellulose, hemicellulose and lignin by the formation of different types of interactions such as hydrogen bond, dipole-dipole and Van der Waals forces. These interactions help treat lignocellulosic biomass to different fractionation [90]. However, different types of ionic liquid and species of wood influenced the formation of functional groups for the regenerated lignin [91]. Organic acid such as formic acid was studied [71] using wheat straw. They reported that the yield of lignin recovery increased when they applied higher temperature and longer time of reaction. When the extraction was induced by these two factors, lignin was dissolved by acid-cleavage of α -aryl ether and arylglycerol- β -ether in the lignin macromolecule resulting in more cleavage of bonds throughout the process. Hydrophilic groups, -OH and -CO and hydrophobic groups, aromatic rings in lignin structure

influenced the good solvent for delignification process [65]. Hydrolysis process to separate lignin and monosaccharides needs low concentration of mineral acid, high temperature and high energy loading to achieve successful separation process.

4.0 APPLICATION OF LIGNIN AND ITS DERIVATIVES

Lignin has many different applications today and it is slowly growing in our industrial market (Table 4). The effort to transform lignin into valuable products for a growing market is importantly needed. The variety of inherent structural in biomass lignin made it useful for the other applications which might brought the structural changes through various chemical modifications for synthesizing different types of lignin to suit the future wider applications [89]. Lignin has been widely used in various industrial applications such as metal ion removal and biosorbent, corrosion inhibitor, antioxidant and antimicrobial, morphological effect, phenolic resin, aviation fuel, and vanillin production.

4.1 Metal Ion Removal and Biosorbent

Lignin can be used in assisting metal adsorption in water pollutions treatment by hazardous metal ions such as nickel (II), cadmium (II), plumbum (II) and Copper (II). The presence of these types of metal ions can cause numerous diseases and disorders to human body such as lung cancer, chronic bronchitis, pulmonary fibrosis besides having significant carcinogenic properties. The presence of functional groups on the lignin surface such as carboxylic and phenolic groups results in a good combination of precursors between oxide groups on the surface of silica. A study by [92] reported that the innovation of SiO₂/lignin hybrid systems (organic/inorganic materials combination) have high surface area, thermal stability and mechanical strength which have the potential to be use as the sorbents metal ions.

The presence of plentiful hydroxyl groups and unique three-dimensional structure of lignin make it an ideal precursor for biosorbent application. Cationization of softwood kraft lignin using glycidyl-trimethylammonium chloride (GTMAC) was used to coagulate and flocculate the negative charged of dyes molecules [93]. This new finding might be used to replace the inorganic coagulants such as ferric chloride, aluminium sulphate and poly aluminium salts which were previously used in high concentrations thus resulting a large volume of sludge. These situations can pose harm to human health. The increase of cationic lignin concentration exceeding the optimal amount overcharged the dyes particles presence in solutions. This extra charged density repels the dyes particles and re-stabilized them in the solutions and later decreased

the amount. In another study, sulfomethylated and oxidized softwood kraft lignin was reported as an anionic flocculant for dye solutions which is highly effected by its charged density. Products with higher charged density performed better than those with lower charged density in removing dyes in solution [94].

Mesoporous lignin-based biosorbent was produced through a sulphur trioxide (SO_3) micro-thermal-explosion process of rice straw which has special structure with the presence of sulfonic functional groups on the surface and large surface area. They provide better diffusion, dispersion and mass transfer behaviour in the field of metal-ions removals such as lead for wastewater treatment [95]. Lignin microspheres was produced by an inverse suspension copolymerization method which provides better adsorption capacity towards lead, Pb (II) in water. A strong binding tendency between basic amine and acidic metal ions are formed due to the presence of abundant functional groups in its structure [96].

Carbon nanotubes (CNTs) have unique properties as sorbents to adsorb different types of pollutants and contaminations in water. However, CNTs is not soluble in water and can easily agglomerate due the presence of strong Van der Waals forces between CNTs bundles and lack of functional groups. Therefore, lignin was chosen as other alternative for the hybridization with CNTs as new nanocomposite and was expected to create large surface area with abundant adsorption active sites by introducing high content of oxygen-containing functional groups that will bind strongly with the contaminants [97]. Besides that, lignin-based hydrogels can also be used as nanocomposites for the same solutions to overcome the toxic pollution. The properties of hydrogels especially their flexibility, elasticity, permeability and ability to absorb huge quantity of water gained the attention of many researchers in order to remove toxic metals from water and wastewater [98].

High density polyethylene (HDPE) was exposed to the degradation process during all stages of its life cycle, starting from the synthesis process, storage and processing to the end. Phenolic compounds present in lignin polyphenols can act as an antioxidant agent to prevent the oxidative degradation in polymers as reported by [99]. They used kraft lignin extracted from black liquor by using three types of acids, hydrochloric acid, HCl, phosphoric acid, H_3PO_4 and acetic acid, CH_3COOH for lignin isolation. Precipitation of lignin by using HCl shows similar characteristics with the Aldrich commercial lignin. They concluded that lignin shows lower antioxidant capacity as compared to the commercial antioxidant. It has higher molecular weight yet still retains its antioxidant behaviour. Behaviour temperature of initial temperature might influenced the product formation.

The addition of lignin extracted from Moso bamboo, Chinese tallow tree wood and switchgrass was reported by [46]. The tensile strength, tensile

modulus and tensile strain of fabrication of polylactic acid (PLA) lignin composites were improved when modified lignin was used compared to the commercial lignin. Acetylation of lignin would modify its surface and thus resulting in the increment of affinity and dispersion of biopolymer which attributes to the higher mechanical properties of bio-based materials.

4.2 Corrosion Inhibitor

The presence of myriads of functional groups in lignin such as phenolic, hydroxyl, carboxyl, benzyl alcohols, methoxyl and aldehyde provide active centres in physical and chemical interactions. The content of oxygen atoms and multiple bonds in alkaline lignin extracted from maple wood adsorbs on the metal surface and forms the barrier between the metal and corrosive environment [100]. Smaller fragments of modified lignin from *Elaeis guineensis* with high phenolic $-\text{OH}$ content (low average molecular weight), antioxidant activity and solubility characteristics shows the improved inhibition process which physically adsorbed onto the mild steel surface [101]. [102] used soda lignin and kraft lignin extracted from oil palm empty fruit bunch to reduce the rust components on the surface of steel formed by ferric-lignin compounds. The oxygen-electron donating groups present in polyphenolic monomers in lignin is expected to adsorb onto the metal surface via the adsorption modes in the media. The lignin efficiency as corrosion inhibitor is related with the number of active sites, molecular sizes, the presence of functional groups and the electron density.

4.3 Antioxidant and Antimicrobial

As a complex phenolic polymer, lignin possesses antimicrobial properties which is highly needed in fabric and textiles industry. The lignin extracted was coated on fabric to be used as potential additional fabric in a sanitary mask. Among the potential used of lignin from sugarcane bagasse is to inhibit and prevent the formation of bacteria, *Staphylococcus epidermis*, the most frequent cause of nosocomial infections on fabric. It is also closely related with skin disorders such as acne vulgaris [103].

[104] reported the potential of lignin as a natural antioxidant additive in food packaging. Polylactic [47] was chosen as its matrix and was blended with lignin by twin screw extrusion and thermos compression. Two types of lignin which contain different phenolic monomer were used, lignin PROTOBIND 100 (extracted from alkali process from a mix of wheat straw and sugarcane) composed 8.0 mg g⁻¹ of phenolic monomers and lignin SARKANDA (extracted from sugarcane) contained 0.5 mg g⁻¹ of phenolic monomers. The immersion of PLA films into the fatty food reflects yielded migration of radical scavengers into the solution by using free radical test, DPPH. Primary radicals from oxygen exist originally in the atmosphere. However, those radicals can be

stimulated either by thermal processing or during the radiation of packaging and food. Those radicals can initiate the lipid oxidation in food. Therefore, antiradical activity of PLA-lignin blend can serve as other alternative to eliminate those radicals.

4.4 Phenolic Resin

Lignin consists many benzene rings resulting in the highest char yield. Its depolymerisation process also leads to the formation of various phenols. Production of value-added chemical such as phenol from lignin produced from enzymatic, weak acid hydrolysis and strong acid hydrolysis process was reported by [105]. [106] used softwood kraft lignin microwave-pyrolysis oil to produce phenol by using switchable hydrophilicity solvents (SHS) method which can be further used in various fields as antioxidants, gasoline additives, food additives, pesticides and colorants. [107] utilized enzymatic hydrolysis (EH) lignin obtained from bio-ethanol production of steam-exploded corn stalk and reported that 50% of phenol in resin was successfully replaced by EH lignin while maintaining the bonding strength of the adhesive. However, the increase of the replacement up to 60% caused the bonding strength to be weaker and failed to meet the Chinese National Standard.

Phenolic resin is a synthetic polymer resulting from the reaction between phenol or substituted phenol with formaldehyde. Lignin can be used to partly replaced phenols in resins production. The used of *Jatropha circus* seed husk lignin which has high quantity of lignin as partial substitute of phenol in phenolic resins shows no changes to their physicochemical properties. However, [108] reported that the substitution of lignin not more than 50% of lignin based on the fractures physical evidence even though it shows the good incorporation in the lignin matrix and best mechanical properties.

Acetosolv process to extract lignin from sugarcane bagasse shows higher thermal stability, low molar mass, constitute major proportion of p-hydroxyphenyl, higher relative phenolic and hydroxyl content, and lower relative methoxyl content compared to kraft lignin. [109] reported on the capability of Japanese cedar (*cryptomeria japonica*) and eucalyptus (*eucalyptus globulus*) to produce lignin-based phenolic resin. The removal of cellulose and hemicellulose were achieved by using the saccharification with formic acid in order to obtain lignin-rich fraction and improve the depolymerization of lignin into phenolic-resin.

Similar application of lignin was studied by [110]. The number of sites in lignin is the vital factor for them to be incorporated with formaldehyde in order to form lignin formaldehyde instead of phenol formaldehyde. Kraft lignin concentration reported in this study is up to 90% which has higher number of activated sites than the other types of lignin. Other than that, kraft lignin composed greater content of phenolic hydroxyl groups even though its

unsubstituted 3- and 5- positions to react with formaldehyde are moderate.

Different types of lignin were reported by [111]. They applied organosolv lignin to replace the phenol incorporated with formaldehyde resin which can be used as an adhesive in the production of particleboard. Unique structure of lignin which consists of many aromatic rings and highly cross-linked structure shows similarity to the network of phenol formaldehyde resins. This intervention may reduce the cost of phenol formaldehyde resins formation since the price of phenol is high apart from being toxic. Besides, organosolv lignin from bamboo (*Phyllosatachys heterocycle*) was also reported by [112]. They reported the successful performance of organosolv lignin from acidic and alkaline of up to 50% substitution of phenol formaldehyde resins synthesis. However, the presence of extractives significantly influenced the synthesis of resin thus the purification step is necessary prior to lignin application. Similar application of lignin-phenol-formaldehyde in plywood was reported by [113] by using lignin extracted from industrial steam exploded wheat straw. Organosolv wheat straw lignin was reported by [114] as a substitution for 50 to 70% of the phenol in a phenol formaldehyde-resol resin and was applied in a plywood manufacturing. The aim to replace the petroleum-derived phenols with phenol-formaldehyde resin from lignocellulosic biomass resources was reported by [115].

4.5 Aviation Fuel

Aviation fuel is a petroleum based-fuel which is produced specifically for powering aircraft. It has special additive fuels compared to less critical applications like heating or road transport to reduce the risk of explosion or icing during the high temperature and different weather. Therefore, application of lignin from renewable biomass in the production of cycloparaffins and aromatics which are partly components in jet fuel production are necessary to reduce our dependence and demand on the fossil energy. [116] used sulphur-free lignin powder derived from wheat straw by catalytic depolymerisation process of lignin which results in C6-C8 aromatics compounds and further converted to C8-C15 aromatics with the alkylation process using ionic liquid. Normally, the commercial and military jet fuels composed of three major components which are paraffin, cycloalkanes and aromatics and the ratio involved in the production process depends on the different types of jets such as Jet-A1, Jet A and JP-8.

Fast pyrolysis of lignin process successfully converted lignocellulosic biomass into bio-oils. However, lignin-derived bio-oils are unable to be directly used as fuel and need to be upgraded to meet the requirement as a jet fuel. One of the approach method reported by [117] is by using Hydrodeoxygenation (HDO) process which produce cyclohexanone as the intermediate lignin-derived

bio-oil and is directly converted into aromatics in the range of jet fuel hydrocarbons. [118] reviewed the production of bio jet fuel from renewable hydrocarbons which has similar properties to jet fuel but more advantages because it contains less sulphur and produces lower carbon dioxide emission.

4.6 Vanillin Production

Serving as the highest volume flavouring agent in food industry, vanillin (4-hydroxy-3-methoxybenzaldehyde) is a major component of natural orchid plant, *Vanilla planifolia*. The expensive price and high time consumption in producing the natural vanillin from orchid plants contribute to the application of renewable resource such as lignin as a substrate to fulfil the higher demand from the

consumer. The lignin oxidation reaction with additional oxygen as the oxidant in batch reactor was reported by [119]. Different types of oxidants were used to produce vanillin from lignin such as nitrobenzene [120, 121], oxygen [121-124], copper oxide [125] copper sulfate [15] and hydrogen peroxide [126]. Lignin was degraded and oxidized, producing vanillin with several types of by-products. The cleavage of the aryl-ether linkages in lignin produced unstable and highly reactive free radicals of low molecular weight products through the rearrangement, electron abstraction and radical-radical interaction. High temperature application around 200-275°C able to degrade the lignin polymeric resulting in formations of aromatic compounds with phenolic groups.

Table 4 Examples of lignin applications

Principle usage	Applications	References
Metal- ion removal and Biosorbent	The presence of sulfonic functional group and large surface area of mesoporous lignin-based-biosorbent allowed better diffusion and better mass transfer behaviour	[46], [92], [93], [95], [96], [98], [99]
Corrosion inhibitor	The presence of varieties of functional groups provide the active site in the interactions between metal surface and lignin as the inhibitor	[100]-[102]
Antioxidant and antimicrobial	Antimicrobial properties of lignin prevent and inhibit bacteria, <i>Staphylococcus epidermis</i> which cause nosocomial infections on fabrics, poly-lactic lignin blend will act as antioxidant in order to protect packed food from light or oxygen	[103], [104]
Phenol-based resin	Replace phenol or substituted phenol in resin production, presence of active site in lignin shows similarity to the network of phenol formaldehyde resin. Presence of benzene ring in lignin structure leads to the depolymerisation process to produce various types of phenol	[105], [108]-[110], [112], [113], [115]
Aviation fuel	Used as part of components production of cycloparaffins and aromatics in jet fuel production	[116]-[118]
Vanillin production	Vanillin can be obtained through the oxidation and degradation of lignin	[119]-[127]

5.0 CONCLUSION

This review paper revealed that lignin has great potential and positive contribution in several different industrial sectors. In addition to its abundancy, the existence of various functional groups and phenolic compounds in lignin structure provide many advantages after being broken into smaller fractions by using the right and effective ways of extraction. Types of extraction method used will determines the quality of the lignin and its derivatives produced which could be efficiently convert to valuable products into future biorefineries. However, utilization of lignin from variable biomass origin requires further research to produce materials which has the same quality with current commercial products.

Conflicts of Interest

The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper.

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References

- [1] Jang, S.-K., Kim, H.-Y., Jeong, H.-S., Kim, J.-Y., Yeo, H., and Choi, I.-G. 2016. Effect of Ethanol Organosolv Pretreatment Factors on Enzymatic Digestibility And Ethanol Organosolv Lignin Structure from *Liriodendron tulipifera* in Specific Combined Severity Factors. *Renewable Energy*. 87: 599-606.
- [2] Cai, J., He, Y., Yu, X., Banks, S. W., Yang, Y., Zhang, X., Yu, Y., Liu, R., and Bridgwater, A. V. 2017. Review of Physicochemical Properties and Analytical Characterization of Lignocellulosic Biomass. *Renewable and Sustainable Energy Reviews*. 76: 309-322.
- [3] Morgan Jr, H. M., Bu, Q., Liang, J., Liu, Y., Mao, H., Shi, A., Lei, H., and Ruan, R. 2017. A Review of Catalytic Microwave Pyrolysis of Lignocellulosic Biomass for Value-added Fuel and Chemicals. *Bioresource Technology*. 230: 112-121.
- [4] Saini, J.K., Saini, R., and Tewari, L. 2015. Lignocellulosic Agriculture Wastes as Biomass Feedstocks for Second-generation Bioethanol Production: Concepts And Recent Developments. *3 Biotech*. 5(4): 337-353.
- [5] Feng, Q. and Lin, Y. 2017. Integrated Processes of Anaerobic Digestion and Pyrolysis for Higher Bioenergy Recovery from lignocellulosic Biomass: A Brief Review. *Renewable and Sustainable Energy Reviews*. 77: 1272-1287.
- [6] Singh, Y. D., Mahanta, P., and Bora, U. 2017. Comprehensive Characterization of Lignocellulosic Biomass through Proximate, Ultimate and Compositional Analysis for Bioenergy Production. *Renewable Energy*. 103: 490-500.
- [7] Sawatdeenarunat, C., Surendra, K., Takara, D., Oechsner, H., and Khanal, S. K. 2015. Anaerobic Digestion of Lignocellulosic Biomass: Challenges and Opportunities. *Bioresource Technology*. 178: 178-186.
- [8] Stefanidis, S. D., Kalogiannis, K. G., Iliopoulou, E. F., Michailof, C. M., Pilavachi, P. A., and Lappas, A. A. 2014. A Study of Lignocellulosic Biomass Pyrolysis via the Pyrolysis of Cellulose, Hemicellulose and Lignin. *Journal of Analytical and Applied Pyrolysis*. 105: 143-150.
- [9] Lu, Y., Lu, Y.-C., Hu, H.-Q., Xie, F.-J., Wei, X.-Y., and Fan, X. 2017. Structural Characterization of Lignin and Its Degradation Products with Spectroscopic Methods. *Journal of Spectroscopy*. 2017.
- [10] Yoo, C. G., Pu, Y., and Ragauskas, A. J. 2017. Ionic Liquids: Promising Green Solvents for Lignocellulosic Biomass Utilization. *Current Opinion in Green and Sustainable Chemistry*. 5: 5-11.
- [11] Pradyawong, S., Qi, G., Li, N., Sun, X. S., and Wang, D. 2017. Adhesion Properties of Soy Protein Adhesives Enhanced by Biomass Lignin. *International Journal of Adhesion and Adhesives*. 75: 66-73.
- [12] Hussin, M. H., Rahim, A. A., Ibrahim, M. N. M., and Brosse, N. 2016. The Capability of Ultrafiltrated Alkaline and Organosolv Oil Palm (*Elaeis guineensis*) Fronds Lignin as Green Corrosion Inhibitor for Mild Steel in 0.5 M HCl solution. *Measurement*. 78: 90-103.
- [13] Movil-Cabrera, O., Rodríguez-Silva, A., Arroyo-Torres, C., and Staser, J. A. 2016. Electrochemical Conversion of Lignin to Useful Chemicals. *Biomass and Bioenergy*. 88: 89-96.
- [14] Beckham, G. T., Johnson, C. W., Karp, E. M., Salvachúa, D., and Vardon, D. R. 2016. Opportunities and Challenges in biological lignin valorization. *Current Opinion in Biotechnology*. 42: 40-53.
- [15] Aarabi, A., Mizani, M., and Honarvar, M. 2017. The Use of Sugar Beet Pulp Lignin for the Production of Vanillin. *International Journal of Biological Macromolecules*. 94: 345-354.
- [16] Fernández-Rodríguez, J., Erdocia, X., Sánchez, C., Alriols, M. G., and Labidi, J. 2017. Lignin Depolymerization for Phenolic Monomers Production by Sustainable Processes. *Journal of Energy Chemistry*. 26(4): 622-631.
- [17] Gillgren, T., Hedenström, M., and Jönsson, L. J. 2017. Comparison of Laccase-catalyzed Cross-linking of Organosolv Lignin and Lignosulfonates. *International Journal of Biological Macromolecules*. 105: 438-446.
- [18] Qian, Y., Otsuka, Y., Sonoki, T., Mukhopadhyay, B., Nakamura, M., Jellison, J., and Goodell, B. 2016. Engineered Microbial Production of 2-pyrone-4, 6-Dicarboxylic Acid from Lignin Residues for Use as an Industrial Platform Chemical. *BioResources*. 11(3): 6097-6109.
- [19] Naseem, A., Tabasum, S., Zia, K. M., Zuber, M., Ali, M., and Noreen, A. 2016. Lignin-derivatives based Polymers, Blends and Composites: A Review. *International Journal of Biological Macromolecules*. 93: 296-313.
- [20] Saberikah, E., Mohammadi-Rovshandeh, J., and Mamaghani, M. 2013. Spectroscopic Comparison of Organosolv Lignins Isolated from Wheat Straw. *Cell. Chem. Technol.* 47(5-6): 40-418.
- [21] Hidajat, M. J., Riaz, A., Park, J., Insyani, R., Verma, D., and Kim, J. 2017. Depolymerization of Concentrated Sulfuric Acid Hydrolysis Lignin to High-yield aromatic Monomers in Basic Sub-and Supercritical Fluids. *Chemical Engineering Journal*. 317: 9-19.
- [22] Pushkin, S. A., Kozlova, L. V., Makarov, A. A., Grachev, A. N., and Gorshkova, T. A. 2015. Cell Wall Components in Torrefied Softwood and Hardwood Samples. *Journal of Analytical and Applied Pyrolysis*. 116: 102-113.
- [23] Custodis, V. B., Bährle, C., Vogel, F., and van Bokhoven, J. A. 2015. Phenols and Aromatics from Fast Pyrolysis of Various Prepared Lignins from Hard- and Softwoods. *Journal of Analytical and Applied Pyrolysis*. 115: 214-223.
- [24] Anwar, Z., Gulfranz, M., and Irshad, M. 2014. Agro-industrial Lignocellulosic Biomass a Key to Unlock the Future Bio-energy: A Brief Review. *Journal of Radiation Research and Applied Sciences*. 7(2): 163-173.
- [25] Isikgor, F. H. and Becer, C. R. 2015. Lignocellulosic Biomass: a Sustainable Platform for the Production of Bio-based Chemicals and Polymers. *Polymer Chemistry*. 6(25): 4497-4559.
- [26] Pathak, S. and Chaudhary, H. 2013. Perspective of Microbial Species used in Lignocelluloses Bioconversion. *Cellulose*. 35: 50.
- [27] Nazir, M. S., Wahjoedi, B. A., Yussof, A. W., and Abdullah, M. A. 2013. Eco-friendly Extraction and Characterization of Cellulose from Oil Palm Empty Fruit Bunches. *BioResources*. 8(2): 2161-2172.
- [28] Maniet, G., Schmetz, Q., Jacquet, N., Temmerman, M., Gofflot, S., and Richel, A. 2017. Effect of Steam Explosion Treatment on Chemical Composition and Characteristic of Organosolv Fescue Lignin. *Industrial Crops and Products*. 99: 79-85.
- [29] Ghaffar, S. H. and Fan, M. 2013. Structural Analysis for Lignin Characteristics in Biomass Straw. *Biomass and Bioenergy*. 57: 264-279.
- [30] Sannigrahi, P., Miller, S. J., and Ragauskas, A. J. 2010. Effects of Organosolv Pretreatment and Enzymatic Hydrolysis on Cellulose Structure and Crystallinity in Loblolly Pine. *Carbohydrate Research*. 345(7): 965-970.
- [31] Gismatulina, Y. A. and Budaeva, V. V. 2017. Chemical Composition of Five *Miscanthus sinensis* Harvests and Nitric-acid Cellulose Therefrom. *Industrial Crops and Products*. 109: 227-232.
- [32] Morales, L. O., Iakovlev, M., Martin-Sampedro, R., Rahikainen, J. L., Laine, J., van Heiningen, A., and Rojas, O. J. 2014. Effects of Residual Lignin and Heteropolysaccharides on the Bioconversion of Softwood Lignocellulose Nanofibrils Obtained by SO₂-ethanol-water Fractionation. *Bioresource Technology*. 161: 55-62.
- [33] Yedro, F. M., Grénman, H., Rissanen, J. V., Salmi, T., Garcia-Serna, J., and Cocero, M. J. 2017. Chemical Composition and Extraction Kinetics of Holm Oak (*Quercus ilex*)

- Hemicelluloses using Subcritical Water. *The Journal of Supercritical Fluids*. 129: 56-62.
- [34] Ciolacu, D., Ciolacu, F., and Popa, V. I. 2011. Amorphous Cellulose—structure and Characterization. *Cellulose Chemistry and Technology*. 45(1): 13.
- [35] Richter, A. P., Brown, J. S., Bharti, B., Wang, A., Gangwal, S., Houck, K., Hubal, E. A. C., Paunov, V. N., Stoyanov, S. D., and Velev, O. D. 2015. An Environmentally Benign Antimicrobial Nanoparticle based on a Silver-infused Lignin Core. *Nature Nanotechnology*. 10(9): 817.
- [36] Matsushita, Y. 2015. Conversion of Technical Lignins to Functional Materials with Retained Polymeric Properties. *Journal of Wood Science*. 61(3): 230.
- [37] Hatakeyama, H. and Hatakeyama, T. 2009. Lignin Structure, Properties, and Applications. *Biopolymers*. Springer. 1-63.
- [38] She, D., Nie, X., Xu, F., Geng, Z., Jia, H., Jones, G., and Baird, M. 2012. Physico-chemical characterization of different alcohol-soluble lignins from rice straw. *Cellulose Chemistry and Technology*. 46(3): 207.
- [39] Medina, J. D. C., Woiciechowski, A. L., Zandona Filho, A., Bissoqui, L., Nosedá, M. D., de Souza Vandenberghe, L. P., Zawadzki, S. F., and Soccol, C. R. 2016. Biological Activities and Thermal Behavior of Lignin from Oil Palm Empty Fruit Bunches as Potential Source of Chemicals of Added Value. *Industrial Crops and Products*. 94: 630-637.
- [40] Xu, C., Arancon, R. A. D., Labidi, J., and Luque, R. 2014. Lignin Depolymerisation Strategies: Towards Valuable Chemicals and Fuels. *Chemical Society Reviews*. 43(22): 7485-7500.
- [41] Prieur, B., Meub, M., Wittermann, M., Klein, R., Bellayer, S., Fontaine, G., and Bourbigot, S. 2017. Phosphorylation of Lignin: Characterization and Investigation of the Thermal Decomposition. *RSC Advances*. 7(27): 16866-16877.
- [42] Zakzeski, J., Buijninx, P. C., Jongerius, A. L., and Weckhuysen, B. M. 2010. The Catalytic Valorization of Lignin for the Production of Renewable Chemicals. *Chemical Reviews*. 110(6): 3552-3599.
- [43] Agrawal, A., Kaushik, N., and Biswas, S. 2014. Derivatives and Applications of Lignin—An insight. *The SciTech Journal*. 1(7): 30-36.
- [44] Li, Q., Gao, Y., Wang, H., Li, B., Liu, C., Yu, G., and Mu, X. 2012. Comparison of Different Alkali-based Pretreatments of Corn Stover for Improving Enzymatic Saccharification. *Bioresource Technology*. 125: 193-199.
- [45] Si, S., Chen, Y., Fan, C., Hu, H., Li, Y., Huang, J., Liao, H., Hao, B., Li, Q., and Peng, L. 2015. Lignin Extraction Distinctively Enhances Biomass Enzymatic Saccharification in Hemicelluloses-rich Miscanthus Species under Various Alkali and Acid Pretreatments. *Bioresource Technology*. 183: 248-254.
- [46] Xie, J., Hse, C. Y., Shupe, T. F., and Hu, T. 2015. Physicochemical Characterization of Lignin Recovered from Microwave-assisted Delignified Lignocellulosic Biomass for Use in Biobased Materials. *Journal of Applied Polymer Science*. 132(40).
- [47] Harman-Ware, A. E., Crocker, M., Pace, R. B., Placido, A., Morton, S., and DeBolt, S. 2015. Characterization of Endocarp Biomass and Extracted Lignin using Pyrolysis and Spectroscopic Methods. *BioEnergy Research*. 8(1): 350-368.
- [48] Li, M.-F., Sun, S.-N., Xu, F., and Sun, R.-C. 2012. Microwave-assisted Organic Acid Extraction of Lignin from Bamboo: Structure and Antioxidant Activity Investigation. *Food Chemistry*. 134(3): 1392-1398.
- [49] Guerra, A., Filpponen, I., Lucia, L. A., Saquing, C., Baumberg, S., and Argyropoulos, D. S. 2006. Toward a Better Understanding of the Lignin Isolation Process from Wood. *Journal of Agricultural and Food Chemistry*. 54(16): 5939-5947.
- [50] Lai, C., Tu, M., Shi, Z., Zheng, K., Olmos, L. G., and Yu, S. 2014. Contrasting Effects of Hardwood and Softwood Organosolv Lignins on Enzymatic Hydrolysis of Lignocellulose. *Bioresource Technology*. 163: 320-327.
- [51] Hatfield, R. and Fukushima, R. S. 2005. Can Lignin be Accurately Measured? *Crop Science*. 45(3): 832-839.
- [52] Fukushima, R. S., Kerley, M. S., Ramos, M. H., Porter, J. H., and Kallenbach, R. L. 2015. Comparison of Acetyl Bromide Lignin with Acid Detergent Lignin and Klason Lignin and Correlation with In Vitro Forage Degradability. *Animal Feed Science and Technology*. 201: 25-37.
- [53] Lee, S. H., Doherty, T. V., Linhardt, R. J., and Dordick, J. S. 2009. Ionic Liquid-mediated Selective Extraction of Lignin from Wood Leading to Enhanced Enzymatic Cellulose Hydrolysis. *Biotechnology and Bioengineering*. 102(5): 1368-1376.
- [54] Espinoza-Acosta, J. L., Torres-Chávez, P. I., Carvajal-Millán, E., Ramírez-Wong, B., Bello-Pérez, L. A., and Montaño-Leyva, B. 2014. Ionic Liquids and Organic Solvents for Recovering Lignin from Lignocellulosic Biomass. *BioResources*. 9(2): 3660-3687.
- [55] Oghbaie, M., Mirshokraie, S., Massoudi, A., and Partovi, T. 2014. Extraction Of Lignins Using A Modified Dioxane Method and an Ionic Liquid and Comparative Molecular Weight and Structural Studies by Chromatography and ¹³C NMR Spectroscopy Techniques. *Journal of Modern Chemistry*. 2(5): 36-40.
- [56] Sidik, D. A. B., Ngadi, N., and Amin, N. A. S. 2013. Optimization of Lignin Production from Empty Fruit Bunch via Liquefaction with Ionic Liquid. *Bioresource Technology*. 135: 690-696.
- [57] Fu, D., Mazza, G., and Tamaki, Y. 2010. Lignin Extraction from Straw by Ionic Liquids and Enzymatic Hydrolysis of the Cellulosic Residues. *Journal of Agricultural and Food Chemistry*. 58(5): 2915-2922.
- [58] Ma, H.-H., Zhang, B.-X., Zhang, P., Li, S., Gao, Y.-F., and Hu, X.-M. 2016. An Efficient Process for Lignin Extraction and Enzymatic Hydrolysis of Corn Stalk by Pyrrolidonium Ionic Liquids. *Fuel Processing Technology*. 148: 138-145.
- [59] Underkofler, K. A., Teixeira, R. E., Pietsch, S. A., Knapp, K. G., and Raines, R. T. 2015. Separation of Lignin from Corn Stover Hydrolysate with Quantitative Recovery of Ionic Liquid. *ACS Sustainable Chemistry & Engineering*. 3(4): 606-613.
- [60] Dibble, D. C., Li, C., Sun, L., George, A., Cheng, A., Çetinkol, Ö. P., Benke, P., Holmes, B. M., Singh, S., and Simmons, B. A. 2011. A Facile Method for the Recovery of Ionic Liquid and Lignin from Biomass Pretreatment. *Green Chemistry*. 13(11): 3255-3264.
- [61] Hansen, B., Kusch, P., Schulze, M., and Kamm, B. 2016. Qualitative and Quantitative Analysis of Lignin Produced from Beech Wood by Different Conditions of the Organosolv Process. *Journal of Polymers and the Environment*. 24(2): 85-97.
- [62] Lu, Q., Liu, W., Yang, L., Zu, Y., Zu, B., Zhu, M., Zhang, Y., Zhang, X., Zhang, R., and Sun, Z. 2012. Investigation of the Effects of Different Organosolv Pulping Methods on Antioxidant Capacity and Extraction Efficiency of Lignin. *Food Chemistry*. 131(1): 313-317.
- [63] Montel-Rivera, F., Huang, G.H., Paquet, L., Deschamps, S., Beaulieu, C., and Hawari, J. 2012. Microwave-assisted Extraction of Lignin from Triticale Straw: Optimization and Microwave Effects. *Bioresource Technology*. 104: 775-782.
- [64] Watkins, D., Nuruddin, M., Hosur, M., Tcherbi-Narteh, A., and Jeelani, S. 2015. Extraction and Characterization of Lignin from Different Biomass Resources. *Journal of Materials Research and Technology*. 4(1): 26-32.
- [65] Ye, Y., Liu, Y., and Chang, J. 2014. Application of Solubility Parameter Theory to Organosolv Extraction of Lignin from Enzymatically Hydrolyzed Cornstalks. *BioResources*. 9(2): 3417-3427.
- [66] Guo, G., Li, S., Wang, L., Ren, S., and Fang, G. 2013. Separation and Characterization of Lignin from Bio-ethanol Production Residue. *Bioresource Technology*. 135: 738-741.
- [67] Manara, P., Zabaniofou, A., Vanderghem, C., and Richel, A. 2014. Lignin Extraction from Mediterranean Agrowastes: Impact of Pretreatment Conditions on Lignin

- Chemical Structure and Thermal Degradation Behavior. *Catalysis Today*. 223: 25-34.
- [68] de la Torre, M. J., Moral, A., Hernández, M. D., Cabeza, E., and Tijero, A. 2013. Organosolv Lignin for Biofuel. *Industrial Crops and Products*. 45: 58-63.
- [69] Cybulska, I., Brudecki, G., Rosentrater, K., Julson, J. L., and Lei, H. 2012. Comparative Study of Organosolv Lignin Extracted from Prairie Cordgrass, Switchgrass and Corn Stover. *Bioresource Technology*. 118: 30-36.
- [70] Patrícia, M., Lino, J., Duarte, L. C., Roseiro, L., Boeriu, C. G., Pereira, H., and Carvalheiro, F. 2015. Fractionation of Hemicelluloses and Lignin from Rice Straw by Combining Autohydrolysis and Optimised Mild Organosolv Delignification. *BioResources*. 10: 2626-2641.
- [71] Zhang, A., Lu, F., Sun, R.-C., and Ralph, J. 2010. Isolation of Cellulolytic Enzyme Lignin from Wood Preswollen/dissolved in Dimethyl sulfoxide/N-methylimidazole. *Journal of Agricultural and Food Chemistry*. 58(6): 3446-3450.
- [72] Rencoret, J., Prinsen, P., Gutiérrez, A., Martínez, A.n.T., and del Río, J. C. 2015. Isolation and Structural Characterization of the Milled Wood Lignin, Dioxane Lignin, and Cellulolytic Lignin Preparations from Brewer's Spent Grain. *Journal of Agricultural and Food Chemistry*. 63(2): 603-613.
- [73] Lai, L. W., Idris, A., and Yusof, N. M. 2014. Lignin Extraction from Oil Palm Trunk by Microwave-alkali Technique. *Malaysian Journal of Fundamental and Applied Sciences*. 10(2).
- [74] Jääskeläinen, A., Sun, Y., Argyropoulos, D., Tamminen, T., and Hortling, B. 2003. The Effect of Isolation Method on the Chemical Structure of Residual Lignin. *Wood Science and Technology*. 37(2): 91-102.
- [75] Nakagame, S., Chandra, R. P., Kadla, J. F., and Saddler, J. N. 2011. The Isolation, Characterization and Effect of Lignin Isolated from Steam Pretreated Douglas-Fir on the Enzymatic Hydrolysis of Cellulose. *Bioresource Technology*. 102(6): 4507-4517.
- [76] Horst, D. J., Behainne, J. J. R., de Andrade Júnior, P. P., and Kovaleski, J. L. 2014. An Experimental Comparison of Lignin Yield from the Klason and Willstatter Extraction Methods. *Energy for Sustainable Development*. 23: 78-84.
- [77] Sa'don, N. A., Rahim, A. A., and Hussin, M. H. 2017. The Effect of p-nitrophenol Toward the Structural Characteristics and Antioxidant Activity of Oil Palm Fronds (OPF) Lignin Polymers. *International Journal of Biological Macromolecules*. 98: 701-708.
- [78] Quesada-Medina, J., Lopez-Cremades, F. J., and Olivares-Carrillo, P. 2010. Organosolv Extraction of Lignin from Hydrolyzed Almond Shells and Application of the δ -value Theory. *Bioresource Technology*. 101(21): 8252-8260.
- [79] Sun, N., Rahman, M., Qin, Y., Maxim, M. L., Rodríguez, H., and Rogers, R. D. 2009. Complete Dissolution and Partial Delignification of Wood in the Ionic Liquid 1-ethyl-3-Methylimidazolium Acetate. *Green Chemistry*. 11(5): 646-655.
- [80] Fu, D. and Mazza, G. 2011. Aqueous Ionic Liquid Pretreatment of Straw. *Bioresource Technology*. 102(13): 7008-7011.
- [81] Gordobil, O., Delucis, R., Egúés, I., and Labidi, J. 2015. Kraft Lignin as Filler in PLA to Improve Ductility and Thermal Properties. *Industrial Crops and Products*. 72: 46-53.
- [82] Constant, S., Basset, C., Dumas, C., Di Renzo, F., Robitzer, M., Barakat, A., and Quignard, F. 2015. Reactive Organosolv Lignin Extraction from Wheat Straw: Influence of Lewis Acid Catalysts on Structural and Chemical Properties of Lignins. *Industrial Crops and Products*. 65: 180-189.
- [83] Gabov, K., Gosselink, R. J., Smeds, A. I., and Fardim, P. 2014. Characterization of Lignin Extracted from Birch Wood by a Modified Hydrotropic Process. *Journal of Agricultural and Food Chemistry*. 62(44): 10759-10767.
- [84] Avelino, F., da Silva, K. T., de Souza, M.d. S. M., Mazzetto, S. E., and Lomonaco, D. 2018. Microwave-assisted Organosolv Extraction of Coconut Shell Lignin by Brønsted and Lewis Acids Catalysts. *Journal of Cleaner Production*. 189: 785-796.
- [85] García, A., Spigno, G., and Labidi, J. 2017. Antioxidant and Biocide Behaviour of Lignin Fractions from Apple Tree Pruning Residues. *Industrial Crops and Products*. 104: 242-252.
- [86] Muhammad, N., Man, Z., Bustam, M. A., Mutalib, M. A., and Rafiq, S. 2013. Investigations of Novel Nitrile-based Ionic Liquids as Pre-treatment Solvent for Extraction of Lignin from Bamboo Biomass. *Journal of Industrial and Engineering Chemistry*. 19(1): 207-214.
- [87] Korotkova, E., Pranovich, A., Wärnä, J., Salmi, T., Murzin, D. Y., and Willför, S. 2015. Lignin Isolation from Spruce Wood with Low Concentration Aqueous Alkali at High Temperature and Pressure: Influence of Hot-Water Pre-Extraction. *Green Chemistry*. 17(11): 5058-5068.
- [88] Lee, R. A., Berberí, V., Labranche, J., and Lavoie, J.-M. 2014. Lignin Extraction–Reassessment of the Severity Factor with Respect to Hydroxide Concentration. *Bioresource Technology*. 169: 707-712.
- [89] Shweta, K. and Jha, H. 2015. Rice Husk Extracted Lignin-TEOS Biocomposites: Effects of Acetylation and Silane Surface Treatments for Application in Nickel Removal. *Biotechnology Reports*. 7: 95-106.
- [90] Mohtar, S. S., Busu, T. N. Z. T. M., Noor, A. M. M., Shaari, N., and Mat, H. 2017. An Ionic Liquid Treatment and Fractionation of Cellulose, Hemicellulose and Lignin from Oil Palm Empty Fruit Bunch. *Carbohydrate Polymers*. 166: 291-299.
- [91] Casas, A., Olié, M., Alonso, M., and Rodríguez, F. 2012. Dissolution of Pinus radiata and Eucalyptus Globulus Woods in Ionic Liquids Under Microwave Radiation: Lignin Regeneration and Characterization. *Separation and Purification Technology*. 97: 115-122.
- [92] Klapiszewski, Ł., Bartczak, P., Wysokowski, M., Jankowska, M., Kabat, K., and Jesionowski, T. 2015. Silica Conjugated with Kraft Lignin and Its Use as a Novel 'Green' sorbent For Hazardous Metal Ions Removal. *Chemical Engineering Journal*. 260: 684-693.
- [93] Kong, F., Parhiala, K., Wang, S., and Fatehi, P. 2015. Preparation of Cationic Softwood Kraft Lignin and Its Application in Dye Removal. *European Polymer Journal*. 67: 335-345.
- [94] He, W., Zhang, Y., and Fatehi, P. 2016. Sulfomethylated Kraft Lignin as a Flocculant for Cationic Dye. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 503: 19-27.
- [95] Xu, F., Zhu, T.-T., Rao, Q.-Q., Shui, S.-W., Li, W.-W., He, H.-B., and Yao, R.-S. 2017. Fabrication of Mesoporous Lignin-based Biosorbent from Rice Straw and Its Application for Heavy-Metal-Ion Removal. *Journal of Environmental Sciences*. 53: 132-140.
- [96] Ge, Y., Qin, L., and Li, Z. 2016. Lignin Microspheres: An Effective and Recyclable Natural Polymer-based Adsorbent for Lead Ion Removal. *Materials & Design*. 95: 141-147.
- [97] Li, Z., Chen, J., and Ge, Y. 2017. Removal of Lead Ion and Oil Droplet from Aqueous Solution by Lignin-grafted Carbon Nanotubes. *Chemical Engineering Journal*. 308: 809-817.
- [98] Thakur, S., Govender, P. P., Mamo, M. A., Tamulevicius, S., Mishra, Y. K., and Thakur, V. K. 2017. Progress in Lignin Hydrogels and Nanocomposites for Water Purification: Future Perspectives. *Vacuum*. 146: 342-355.
- [99] Piña, I., Ysambertt, F., Perez, D., and Lopez, K. 2015. Study of Antioxidant Effectiveness of Kraft Lignin in HDPE. *Journal of Polymers*. 2015.
- [100] mnim Altwaiq, A., Sa'ib, J. K., Al-lu'aiibi, S., Lehmann, R., Drücker, H., and Vogt, C. 2011. The Role of Extracted Alkali Lignin as Corrosion Inhibitor. *J. Mater. Environ. Sci.* 2(3): 259-270.
- [101] Hussin, M. H., Rahim, A. A., Ibrahim, M. N. M., and Brosse, N. 2015. Improved Corrosion Inhibition of Mild Steel by Chemically Modified Lignin Polymers from Eleis

- Guineensis Agricultural Waste. *Materials Chemistry and Physics*. 163: 201-212.
- [102] Akbarzadeh, E., Ibrahim, M. M., and Rahim, A. A. 2011. Corrosion Inhibition of Mild Steel in Near Neutral Solution by Kraft and Soda Lignins Extracted from Oil Palm Empty Fruit Bunch. *Int. J. Electrochem. Sci.* 6(11): 5396-5416.
- [103] Sunthornvarabhas, J., Liengprayoon, S., and Suwonsichon, T. 2017. Antimicrobial Kinetic Activities of Lignin from Sugarcane Bagasse for Textile Product. *Industrial Crops and Products*. 109: 857-861.
- [104] Domenek, S., Louaifi, A., Guinault, A., and Baumberger, S. 2013. Potential of Lignins as Antioxidant Additive in Active Biodegradable Packaging Materials. *Journal of Polymers and the Environment*. 21(3): 692-701.
- [105] Kleinert, M. and Barth, T. 2008. Phenols from Lignin. *Chemical Engineering & Technology: Industrial Chemistry-Plant Equipment-Process Engineering-Biotechnology*. 31(5): 736-745.
- [106] Fu, D., Farag, S., Chaouki, J., and Jessop, P. G. 2014. Extraction of Phenols from Lignin Microwave-pyrolysis Oil using a Switchable Hydrophilicity Solvent. *Bioresource technology*. 154: 101-108.
- [107] Qiao, W., Li, S., and Xu, F. 2016. Preparation and Characterization of a Phenol-formaldehyde Resin Adhesive obtained from Bio-ethanol Production Residue. *Polymers & Polymer Composites*. 24(2): 99.
- [108] Vega-Aguilar, C. A., Lutz, G., and Mata-Segreda, J. F. 2015. Phenolic Resin Derived from *Jatropha Curcas* Seed-husk Lignin as Phenol Substitute. *Cuadernos de Investigación UNED*. 7(2): 217-223.
- [109] Muranaka, Y., Nakagawa, H., Hasegawa, I., Maki, T., Hosokawa, J., Ikuta, J., and Mae, K. 2017. Lignin-based Resin Production from Lignocellulosic Biomass Combining Acidic Saccharification and Acetone-water Treatment. *Chemical Engineering Journal*. 308: 754-759.
- [110] Abdelwahab, N. and Nassar, M. 2011. Preparation, Optimisation and Characterisation of Lignin Phenol Formaldehyde Resin as Wood Adhesive. *Pigment & Resin Technology*. 40(3): 169-174.
- [111] Cetin, N. S. and Özmen, N. 2002. Use of Organosolv Lignin In Phenol-formaldehyde Resins for Particleboard Production: I. Organosolv Lignin Modified Resins. *International Journal of Adhesion and Adhesives*. 22(6): 477-480.
- [112] Pang, B., Yang, S., Fang, W., Yuan, T.-Q., Argyropoulos, D. S., and Sun, R.-C. 2017. Structure-property Relationships for Technical Lignins for the Production of Lignin-phenol-formaldehyde Resins. *Industrial Crops and Products*. 108: 316-326.
- [113] Zhao, M., Jing, J., Zhu, Y., Yang, X., Wang, X., and Wang, Z. 2016. Preparation and Performance of Lignin-phenol-formaldehyde Adhesives. *International Journal of Adhesion and Adhesives*. 64: 163-167.
- [114] Tachon, N., Benjelloun-Mlayah, B., and Delmas, M. 2016. Organosolv Wheat Straw Lignin as a Phenol Substitute for Green Phenolic Resins. *BioResources*. 11(3): 5797-5815.
- [115] Pinheiro, F. G. C., Soares, A. K. L., Santaella, S. T., e Silva, L. M. A., Canuto, K. M., Cáceres, C. A., de Freitas Rosa, M., de Andrade Feitosa, J. P., and Leitão, R. C. 2017. Optimization of the Acetosolv Extraction of Lignin from Sugarcane Bagasse for Phenolic Resin Production. *Industrial Crops and Products*. 96: 80-90.
- [116] Bi, P., Wang, J., Zhang, Y., Jiang, P., Wu, X., Liu, J., Xue, H., Wang, T., and Li, Q. 2015. From Lignin to Cycloparaffins and Aromatics: Directional Synthesis of Jet and Diesel Fuel Range Biofuels using Biomass. *Bioresource Technology*. 183: 10-17.
- [117] Saidi, M. and Jahangiri, A. 2017. Refinery Approach of Bio-oils Derived from Fast Pyrolysis of Lignin to Jet Fuel Range Hydrocarbons: Reaction Network Development for Catalytic Conversion of Cyclohexanone. *Chemical Engineering Research and Design*. 121: 393-406.
- [118] Gutiérrez-Antonio, C., Gómez-Castro, F., de Lira-Flores, J., and Hernández, S. 2017. A Review on the Production Processes of Renewable Jet Fuel. *Renewable and Sustainable Energy Reviews*. 79: 709-729.
- [119] Araújo, J. D., Grande, C. A., and Rodrigues, A. E. 2010. Vanillin Production from Lignin Oxidation in a Batch Reactor. *Chemical Engineering Research and Design*. 88(8): 1024-1032.
- [120] Moodley, B., Mulholland, D., and Brookes, H. 2012. The Chemical Oxidation of lignin Found in Sappi Saiccor Dissolving Pulp Mill Effluent. *Water SA*. 38(1): 1-8.
- [121] Tang, P.-L., Hassan, O., Maskat, M. Y., and Badri, K. 2015. Production of Monomeric Aromatic Compounds from Oil Palm Empty Fruit Bunch Fiber Lignin by Chemical and Enzymatic Methods. *BioMed Research International*. 2015.
- [122] Villar, J., Caperos, A., and Garcia-Ochoa, F. 2001. Oxidation of Hardwood Kraft-lignin to Phenolic Derivatives with Oxygen as Oxidant. *Wood Science and Technology*. 35(3): 245-255.
- [123] Pinto, P. C. R., Costa, C. E., and Rodrigues, A. E. 2013. Oxidation of Lignin from Eucalyptus Globulus Pulping Liquors to Produce Syringaldehyde and Vanillin. *Industrial & Engineering Chemistry Research*. 52(12): 4421-4428.
- [124] Shakeri, A., Rad, S. M., and Ghasemian, A. 2013. Oxidative Production of Vanillin from Industrial Lignin using Oxygen and Nitrobenzene: A Comparative Study. *Int J Farming Allied Sci*. 2: 1165-1171.
- [125] Ouyang, X.-p., Tan, Y.-d., and Qiu, X.-q. 2014. Oxidative Degradation of Lignin for Producing Monophenolic Compounds. *Journal of Fuel Chemistry and Technology*. 42(6): 677-682.
- [126] Li, Y., Chang, J., and Ouyang, Y. *Selective Production of Aromatic Aldehydes from Lignin by Metalloporphyrins/H₂O₂ System*. *Advanced Materials Research*. 2013. Trans Tech Publ.
- [127] Ngadi, N., Abdul Halim, N., and Ibrahim, M. 2014. Isolation and Characterization of Vanillin from Coconut Husk Lignin Via Alkaline Nitrobenzene Oxidation. *J Teknol*. 67: 19-23.